

TITLE: Characterization and Fate of Ammonia and Hydrogen Sulfide from Animal Feeding Operations: Their Emissions, Transport, Transformation, Deposition, and Impact on Fine Particulate Matter (PM_{fine})

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Objectives

RESEARCH

- Characterize emissions of ammonia (NH_3) and hydrogen sulfide (H_2S) from lagoon, hog barns, soil and spraying operations; and develop emission factors.
- Formulate exchange of NH_3 and H_2S flux in terms of external properties (physical, chemical, biological status) and atmospheric processes.
- Develop a coupled mass-transfer with chemical reactions, and equilibrium models for H_2S emissions from waste treatment lagoon.
- Estimate deposition velocity and deposition potential for NH_3 and H_2S using micrometeorological and plant ecological measurements.
- Estimate wet deposition potential for ammonium (NH_4^+) and sulfate (SO_4^{2-}); analyze total deposition (wet + dry) at a regional scale; assess its temporal and spatial variability using NADP observations and a regional air quality model.
- Characterize source-receptor relationships between agricultural emissions, and regional studies of N and S based on isotopic studies and back-trajectory analyses.
- Synthesize knowledge gained from emissions measurements and dry depositions of NH_3 and H_2S into a detailed air quality model to diagnose and reduce uncertainties so that reliable estimates of larger scale distributions and process budgets can be simulated.
- Improve current understanding of the cycling of N and S compounds in the atmosphere; investigate coupling of these compounds with atmospheric aerosols and other criteria pollutants through development and evaluation of comprehensive multi-pollutant regional model.
- Characterize and assess air quality in the region.

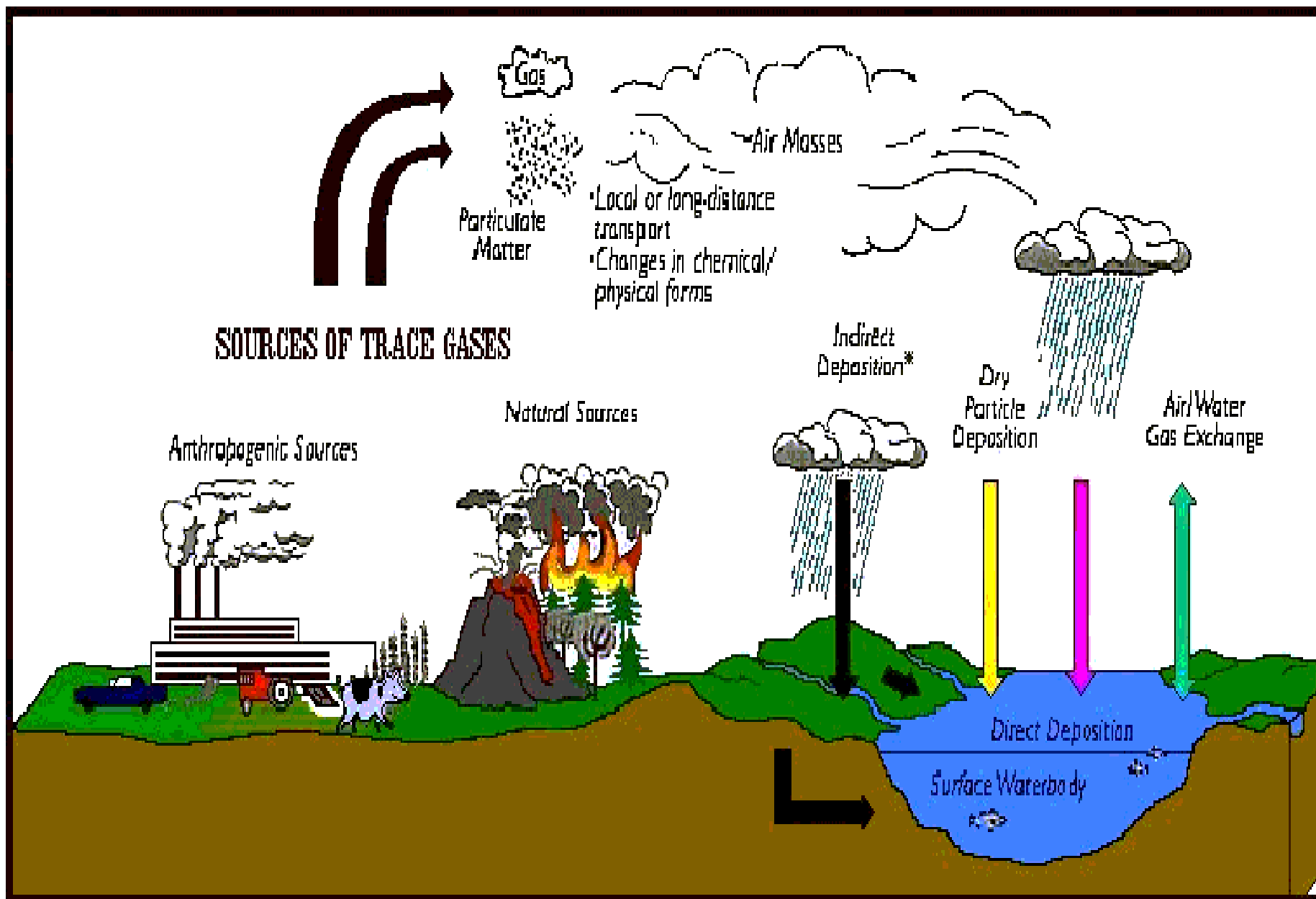
EXTENSION AND EDUCATION

- Improve public understanding of air quality issues related to animal feeding operations, resulting in best management practices (BMPs).
- Incorporate agricultural air quality into new introductory undergraduate/graduate courses.
- Develop and offer courses/short courses on agricultural air quality to the stakeholder community and students.

Student Thesis Topics

- **Jessica Blunden (Ph.D. Summer 2006)** Measurements, modeling, and analysis of ammonia and reduced sulfur compounds at a commercial swine facility in North Carolina
- **Stephen Goetz (M.S. Summer 2005)** Measurement, analysis, and modeling of fine particulate matter in Eastern North Carolina
- **Grace Hendrix (M.S. Summer 2006)** The role of an ammonia rich environment for fine particulate matter formation and transport in North Carolina
- **Stephen Konarik (M.S. Summer 2006)** Relation of dry and wet deposition and precipitation intensities over the southeastern United States
- **Chris Occhipinti (M.S. Summer 2006)** Isotopic classification of source/receptor relationships of nitrogen pollutants in North Carolina.

Atmospheric emissions, transport, transformation & deposition of trace gases



*Indirect deposition is direct deposition to land followed by runoff or seepage through groundwater to a surface water body. (Source: Aneja et al., 2001)

GLOBAL SOURCES OF TROPOSPHERIC AMMONIA

1.	Fossil Fuel Combustion	2 Tg N/Yr
2.	Soil-Biogenic Emissions	
	Cultivated Land	10 Tg N/Yr
	Undisturbed Soils	10 Tg N/Yr
3.	Domestic Animal Waste	32 Tg N/Yr
4.	Human Excretion	4 Tg N/Yr
5.	Biomass Burning	5 Tg N/Yr
6.	Seas and Oceans	13 Tg N/Yr
Total Global Ammonia Emissions		~75 Tg N/Yr

1 Tg = 10^{12} g

Non-Industrial Sources of Sulfur in the Atmosphere (Gmol yr⁻¹)*

Source	Hydrogen sulfide	Dimethyl sulfide	Carbon Disulfide	Carbonyl Sulfide
Oceans	< 9	500-1300	2.4-9.5	2.7-7.8
Coastal Wetlands	0.2-30	0.2-18	0.2-1.2	2.3-7.8
Soils and Plants	2-56	3-24	0.4	-
Volcanoes	16-47	-	0.2-2.4	0.1-1.5
Biomass burning	-	-	-	0.7-4.3
Other	-	-	-	4.5-14.8*
SUMS	18-133	503-1342	3.3-14.1	10.4-37.1

Reaction of OH• with carbon disulfide and dimethyl sulfide

*1 mol = 32g S

1 Gmol = 10⁹ mol

Animal Feeding Operations???

Source: Warneck (2000)

A Few NC Swine Statistics



Year	Population (millions)	# of Farms
1987	~2.5	~13,000
1997	~10	<5,000

**North Carolina is the second leading producer of hogs in the U.S.
Iowa is #1**

1997: NC Moratorium established, hog population

H₂S Accepted Ambient Level (AAL)

Acceptable Ambient Level (AAL)	Time Average	Date of Acceptance
83ppb 0.120 mg m ⁻³	24-hour	April 8, 2004

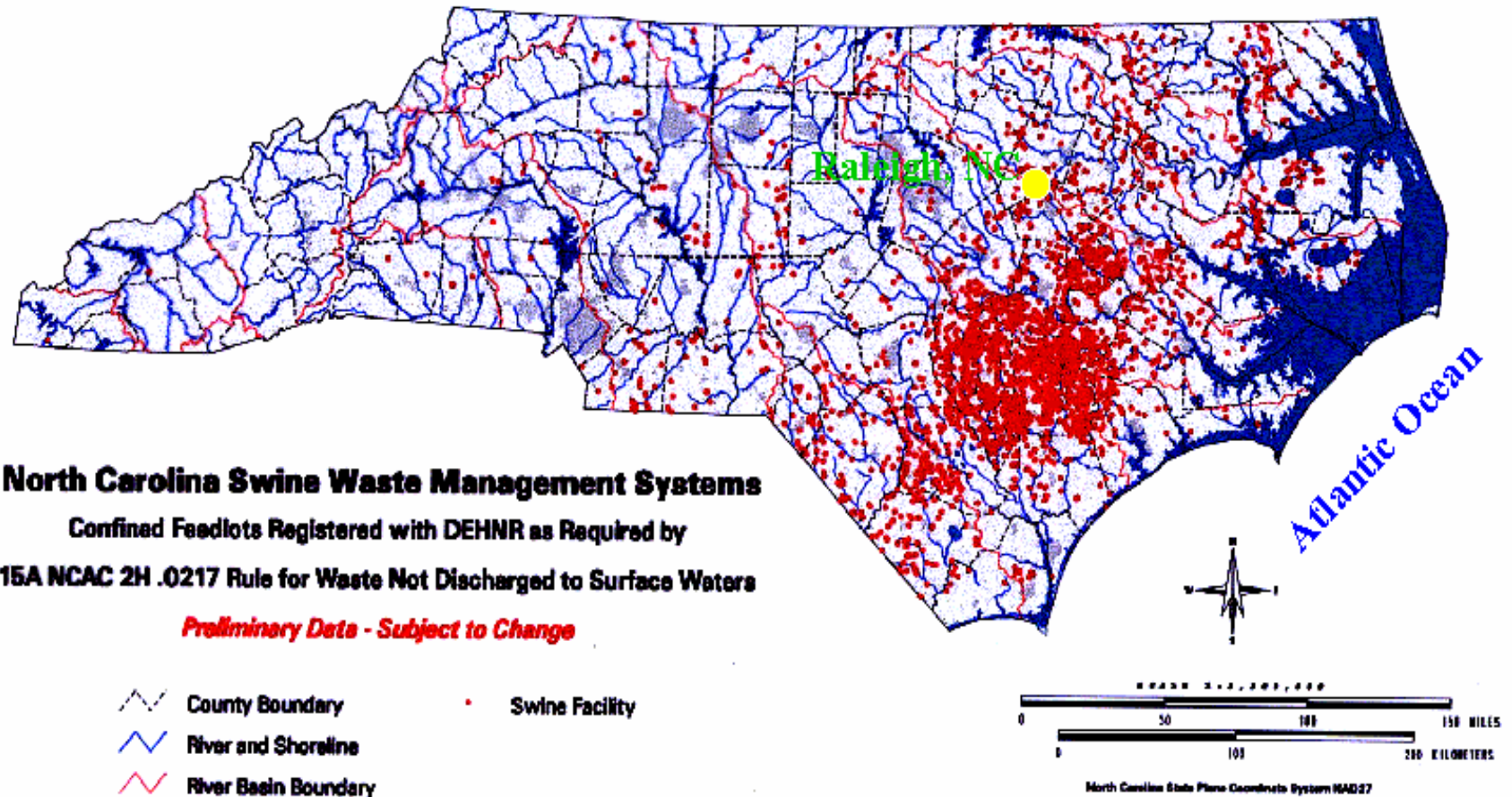
Source: <http://h2o.enr.state.nc.us/admin/emc/2004/documents/2004-04EMCminutes.doc>

Exposure to elevated levels may lead to respiratory and asthmatic problems

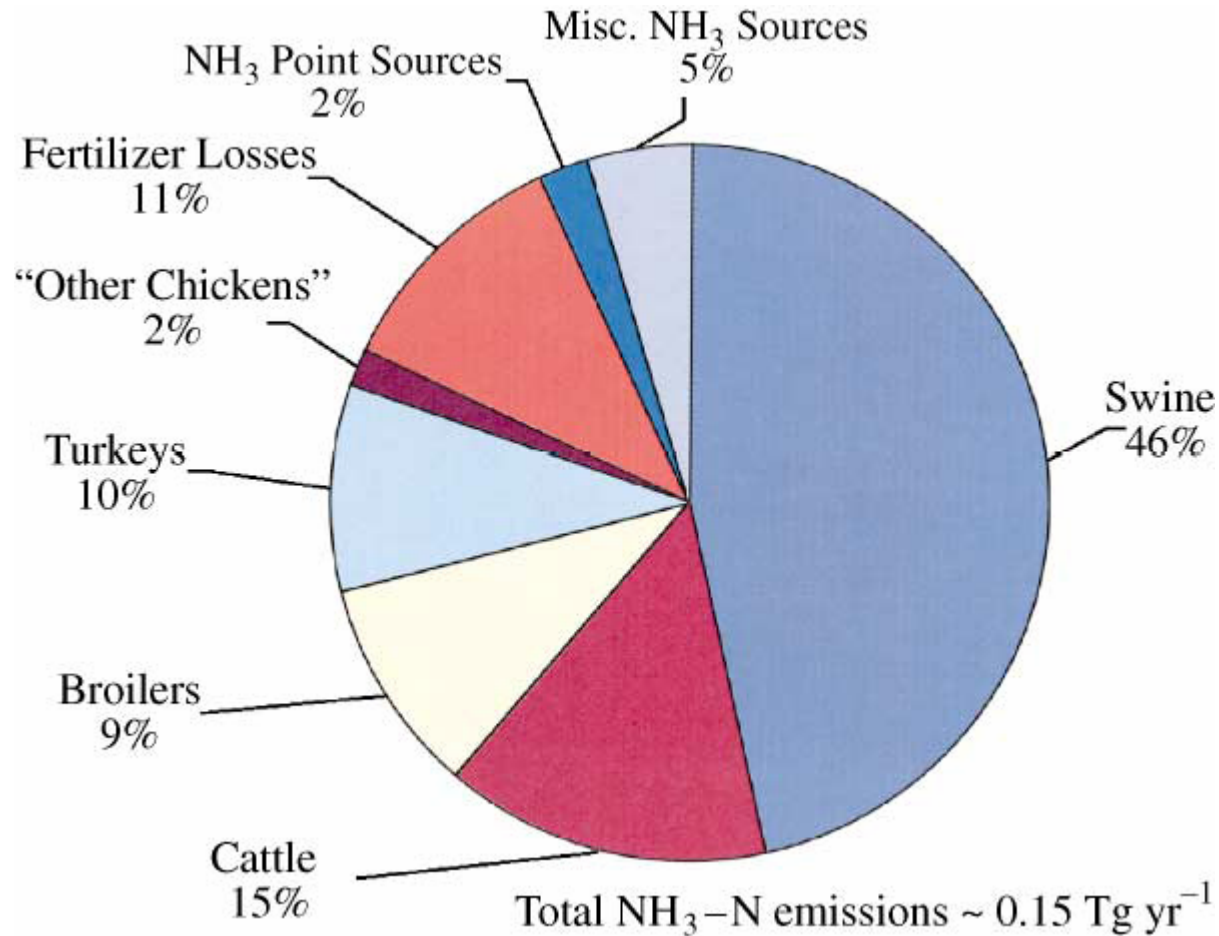
*****There are no federal standards; U.S. EPA does not recognize H₂S as an air toxin*****

Swine Farm Distribution in North Carolina

(2nd in the Nation)

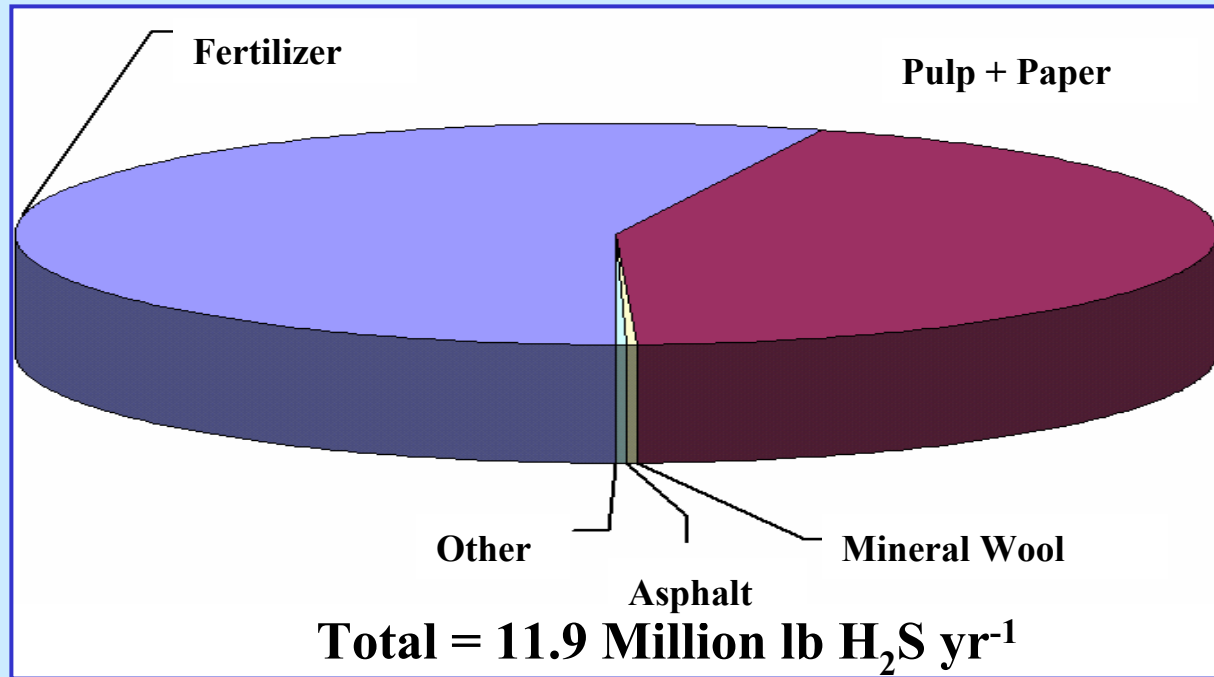


North Carolina NH_3 Emissions Inventory



Source: Aneja et al., 1998

North Carolina 2002 H₂S Emissions Inventory



What about Animal Feeding Operations???

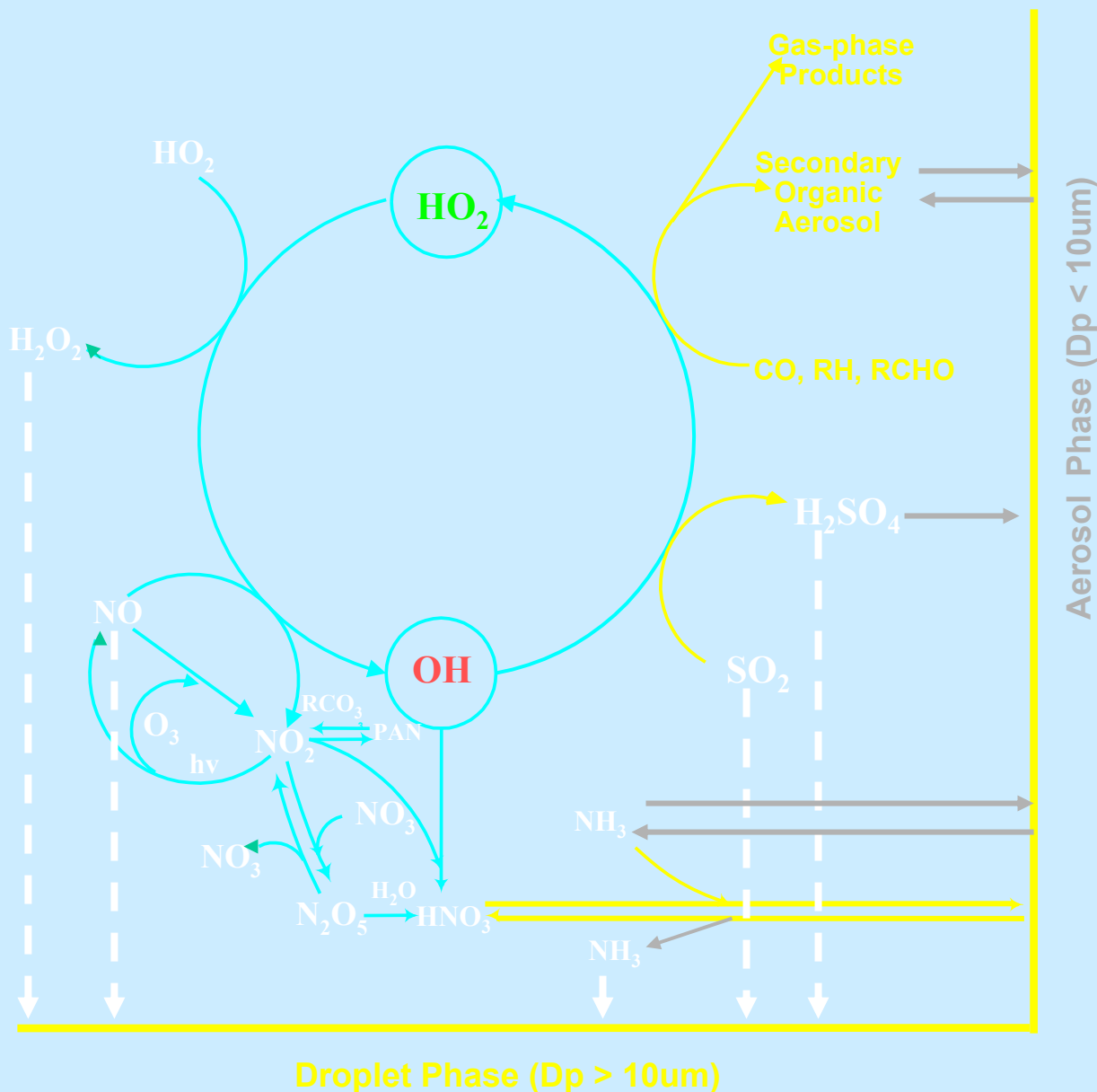
No quality data from previous measurements

U.S. EPA estimates ~40 Million lb H₂S yr⁻¹ in N.C. based on

Midwest farm emission factors (*unpublished data*)

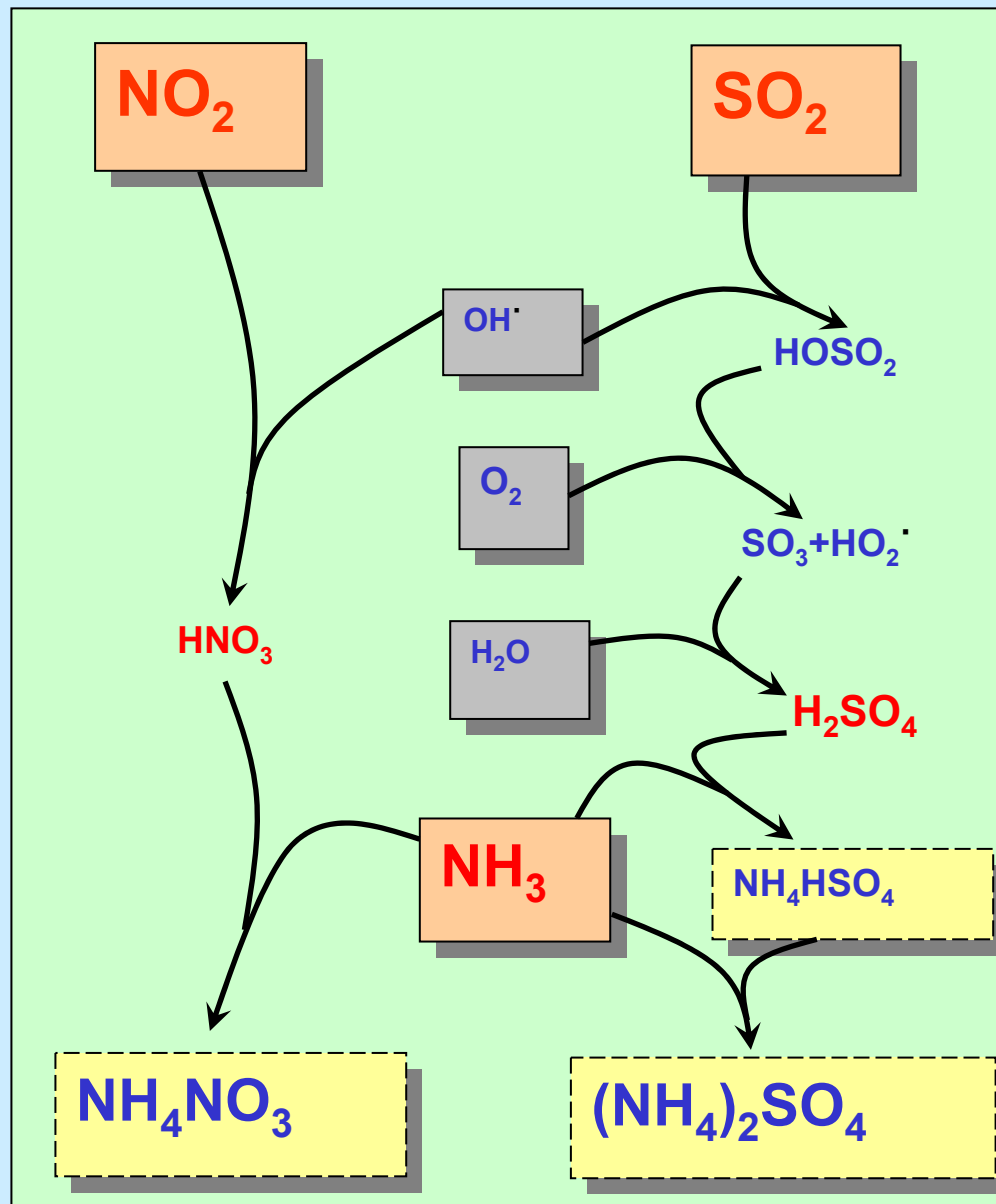
N.C. DAQ believes this is a gross overestimation

Gas-To-Particle Conversion Processes



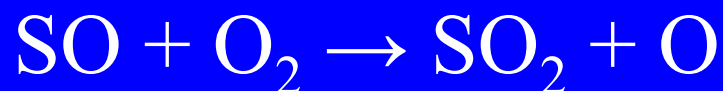
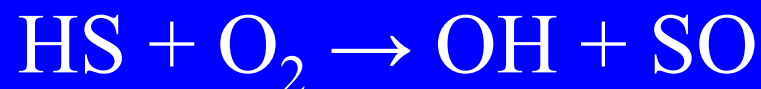
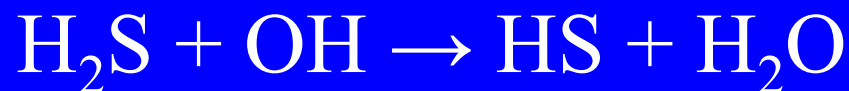
Chemical coupling in the atmospheric gas, particle, and droplet phases (Meng, et al., 1997).

Gas-To-Particle Conversion Processes



(Ronald McCulloch, 1999)

Primary Chemical Reaction for H₂S in the Ambient Atmosphere

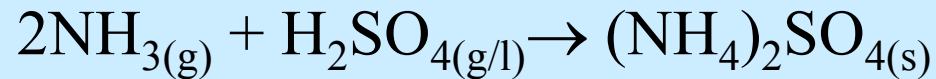
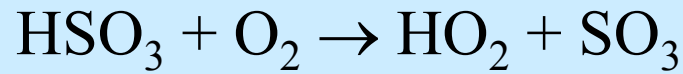


Generally:

Reduced sulfur compound + complex set of atmospheric chemical reactions
→ SO₂ + products

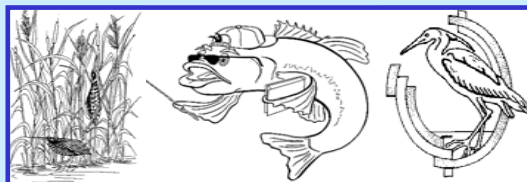
Pathway for Aerosol Formation

Then:



Lifetime of Atmospheric Ammonium Sulfate: ~1-15 days

- **PM_{fine} (Criteria pollutant) may contribute to bronchial or respiratory problems in humans**
- **Deposition of Ammonium Sulfate can contribute to degradation of sensitive plant and water ecosystems**



North Carolina Experimental Research Site

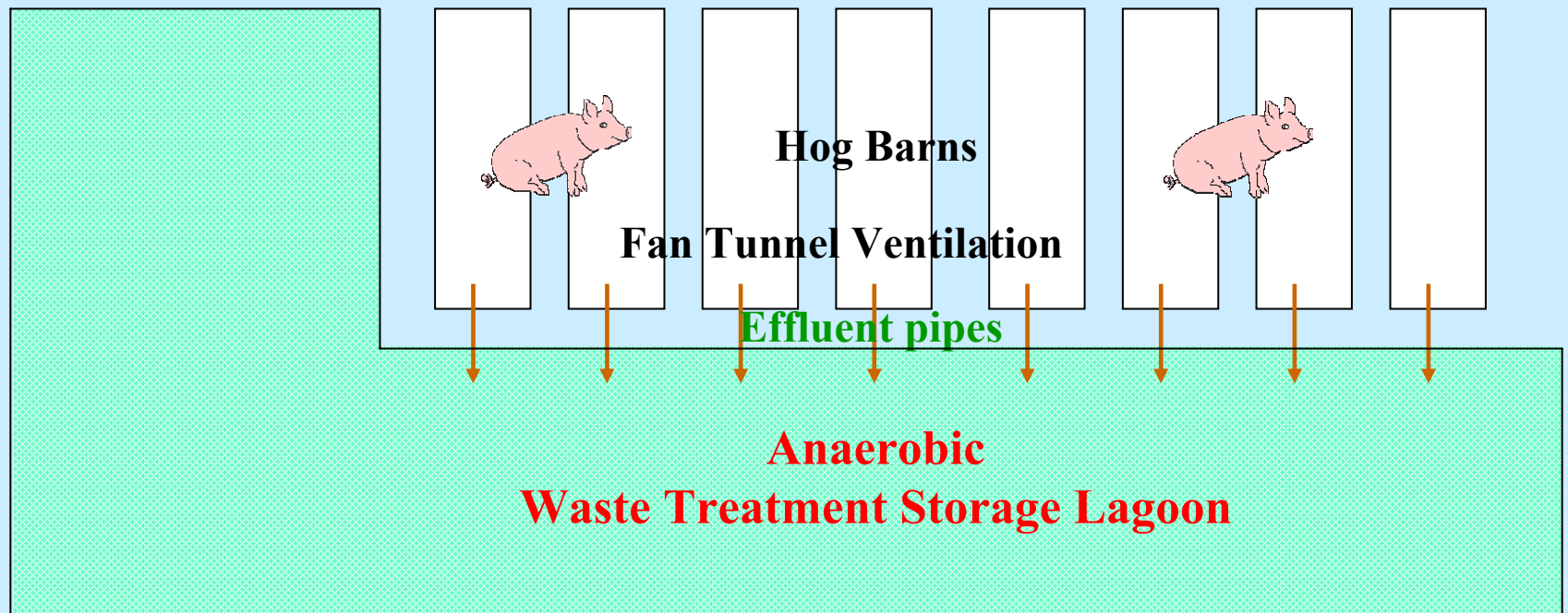


Farm Location

 Jones County

Experimental Site

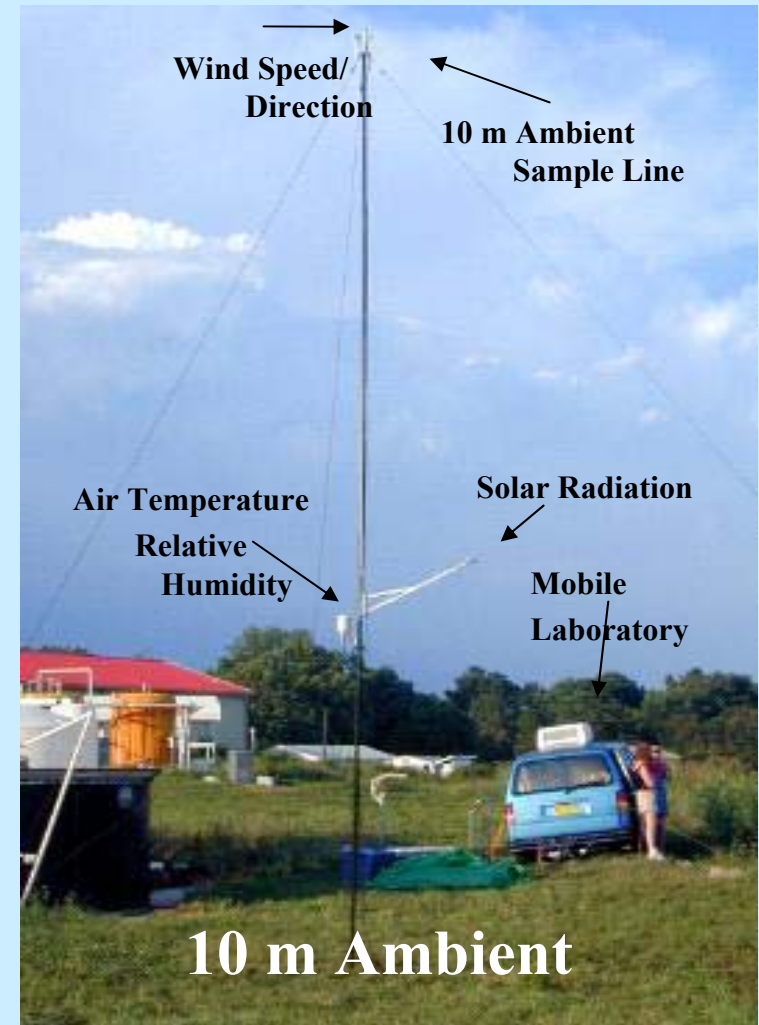
Lagoon & Spray Technology



*Not drawn to scale

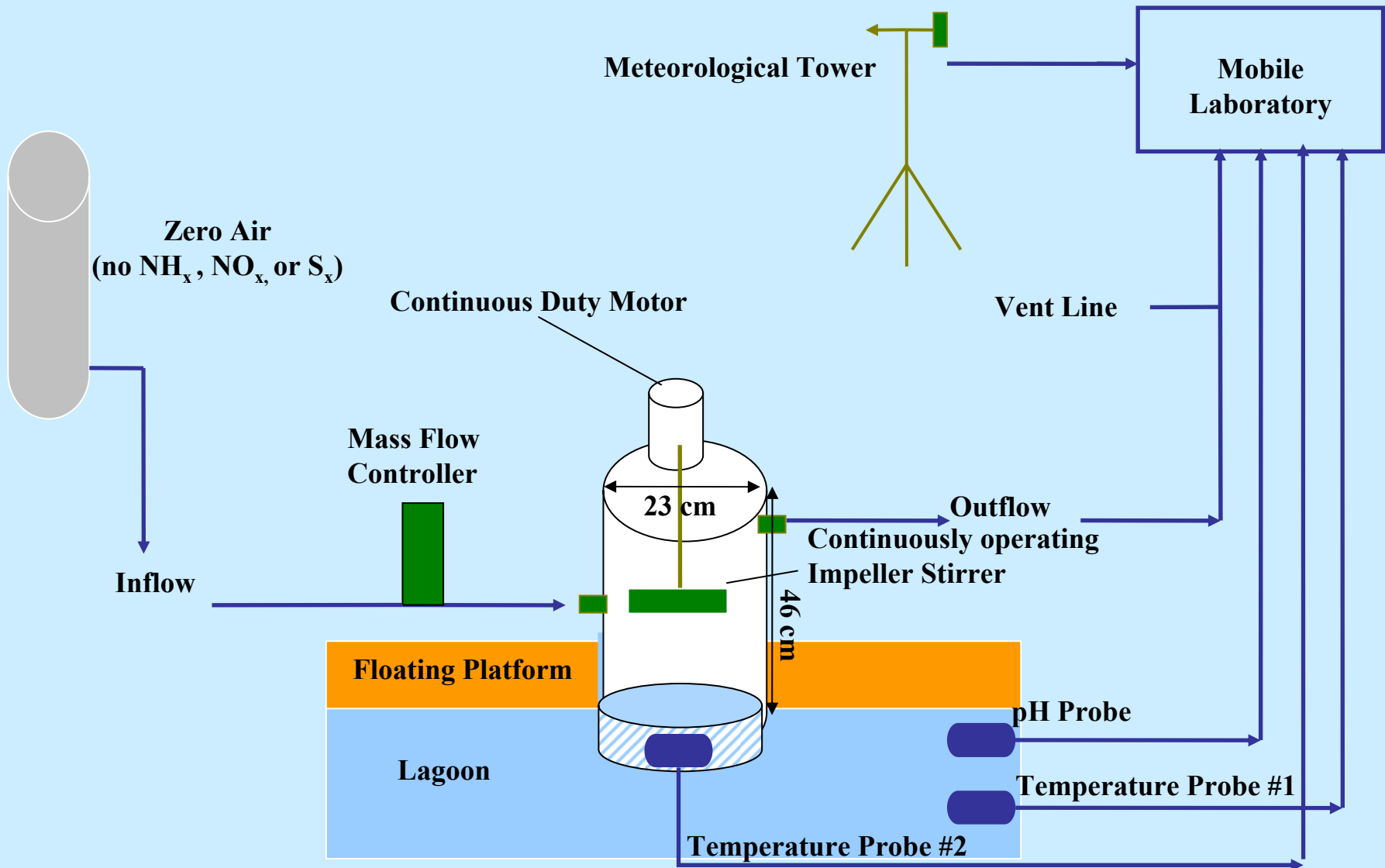
On-site
Agricultural Crops

On-Site Measurement Locations



Dynamic Flow-Through Chamber System

Lagoon and Soil Measurements



Analysis Instrumentation/ Quality Assurance

❖ Continuous NH_3 measurements

- Thermo Environmental Instruments Model 17C chemiluminescence analyzer.
- Calibration prior to and after each field experiment.
- Span checks (80, 60, 40 and 20% of full-scale range), zero air measurements.

❖ Continuous H_2S measurements

- Thermo Environmental Instruments Model 450C pulsed fluorescence $\text{H}_2\text{S}/\text{SO}_2$ analyzer.
- Calibration prior to and after each field experiment.
- Span checks (80, 60, 40 and 20% of full-scale range), zero air measurements.

❖ Data Recorder

- Campbell Scientific CR10X data logger coupled with an AM 16/32 multiplexer collects data every second and averages over 15-minute intervals.
- Records data for H_2S concentration, mass flow controller, and meteorological and lagoon parameters.

❖ Reduced sulfur measurements

H_2S , DMS, DMDS, CS_2 , COS, CH_3SH , $\text{C}_2\text{H}_5\text{SH}$

- Shimadzu Model 14B Gas Chromatograph equipped with a Flame Photometric Detector (GC-FPD).
- Automated sample analysis made once per hour.
- Calibration curves established.
- Minimum detectable limits set for each compound.
- Standards and blanks run to ensure proper identification and concentrations.

Flux Calculations

$$J = C_{H_2S}q$$

Barn emissions

J Flux ($\mu\text{g min}^{-1}$)

C_{H_2S} H_2S concentration ($\mu\text{g m}^{-3}$)

q Fan flow rate ($\text{m}^3 \text{min}^{-1}$) (for each fan running)

$$\frac{J}{h} = C_{eq} \left(\frac{LA_w}{V} + \frac{q}{V} \right)$$

Lagoon and soil emissions

J Flux ($\mu\text{g m}^{-2} \text{min}^{-1}$)

h Chamber height (cm)

C_{eq} Steady-state H_2S concentration ($\mu\text{g m}^{-3}$)

L Loss term (determined experimentally)

A_w Internal chamber wall area (cm^2)

q Flow rate (L min^{-1})

V Volume inside the chamber (L)

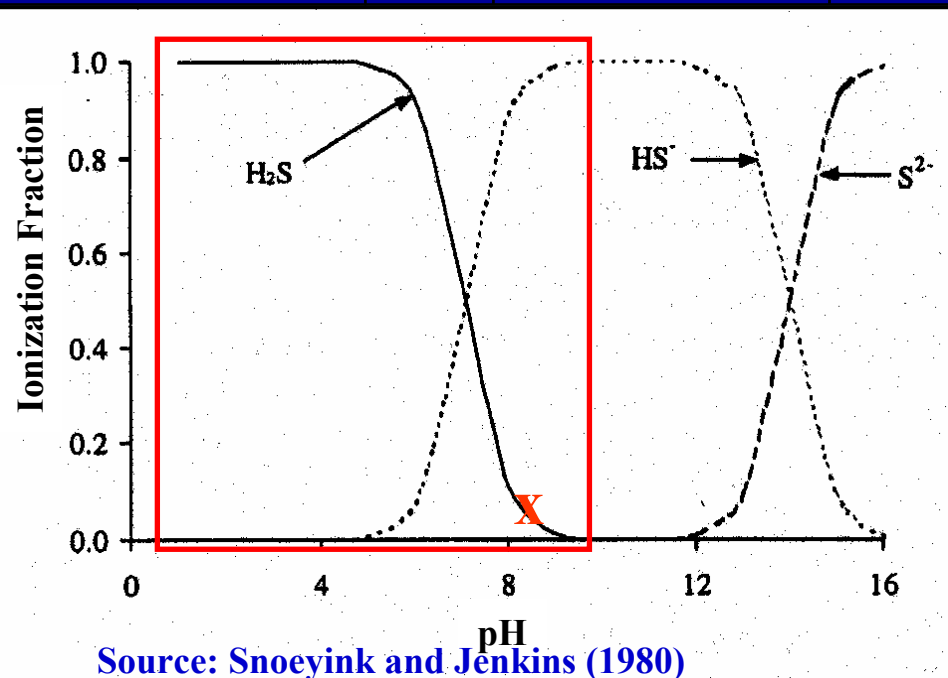
Assumptions:

Steady state $\frac{dC}{dt} = 0$

$R = 0$, $[C]_0 = 0$ when zero grade air is used as carrier gas

Experimental Site Lagoon Parameters

	pH	Lagoon Sfc Temp (°C)	NH _{3(aq)} (mg L ⁻¹)	TKN _(aq) (mg L ⁻¹)	Sulfide _(aq) (mg L ⁻¹)	H ₂ S _(aq) * (mg L ⁻¹)
Oct 25 - Nov 1 (2004)	8.1	18.5	374	406	0.5	0.07
Feb 15 – Feb 22 (2005)	8.1	11.6	489	536	3.7	0.5
Apr 14 – Apr 20 (2005)	7.9	15.0				



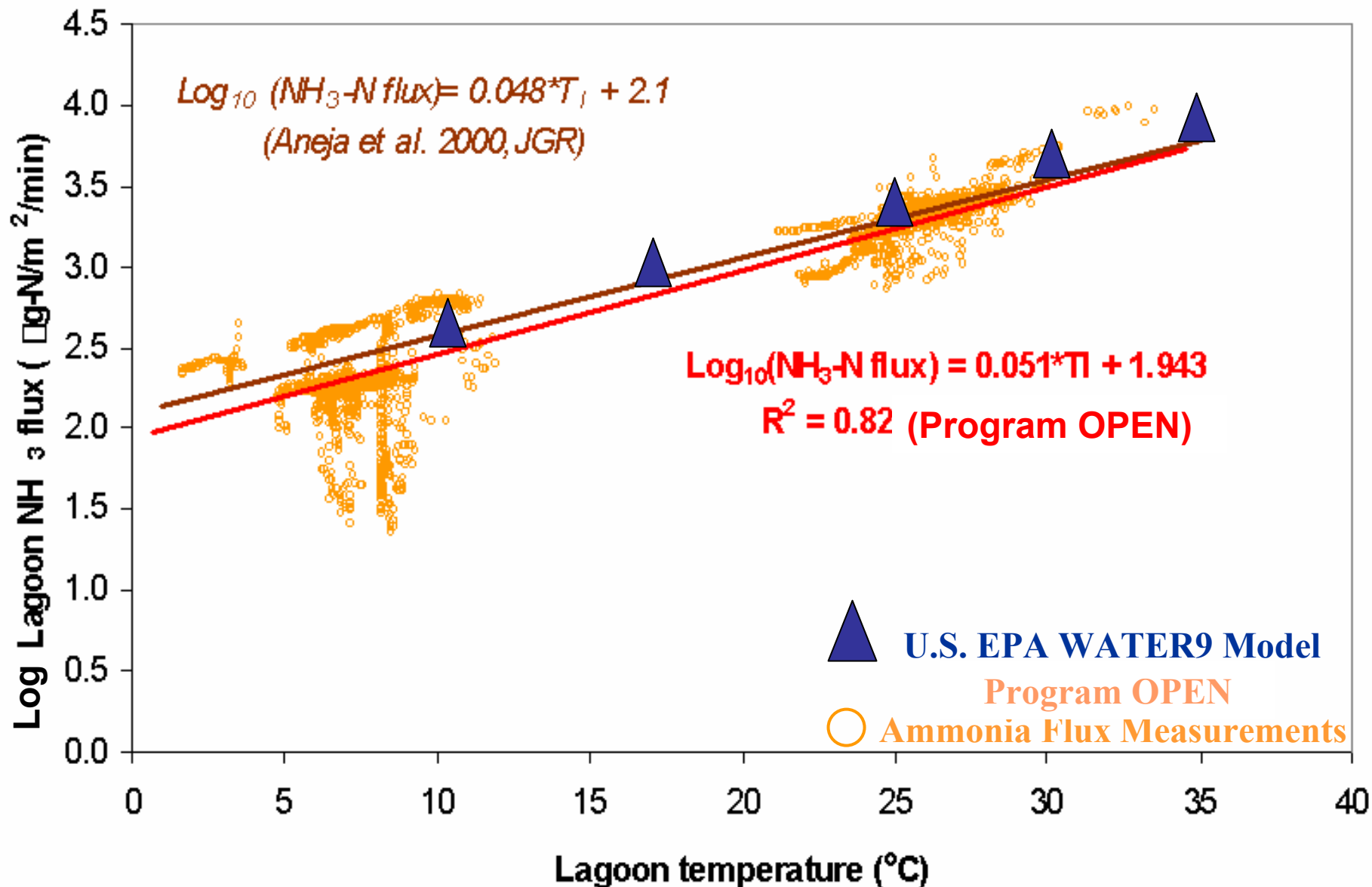
* Calculated Value

For Highest H₂S Emissions:

- ✓ Low lagoon pH
- ✓ High lagoon H₂S_(aq) concentration
- ✓ High lagoon surface temperature

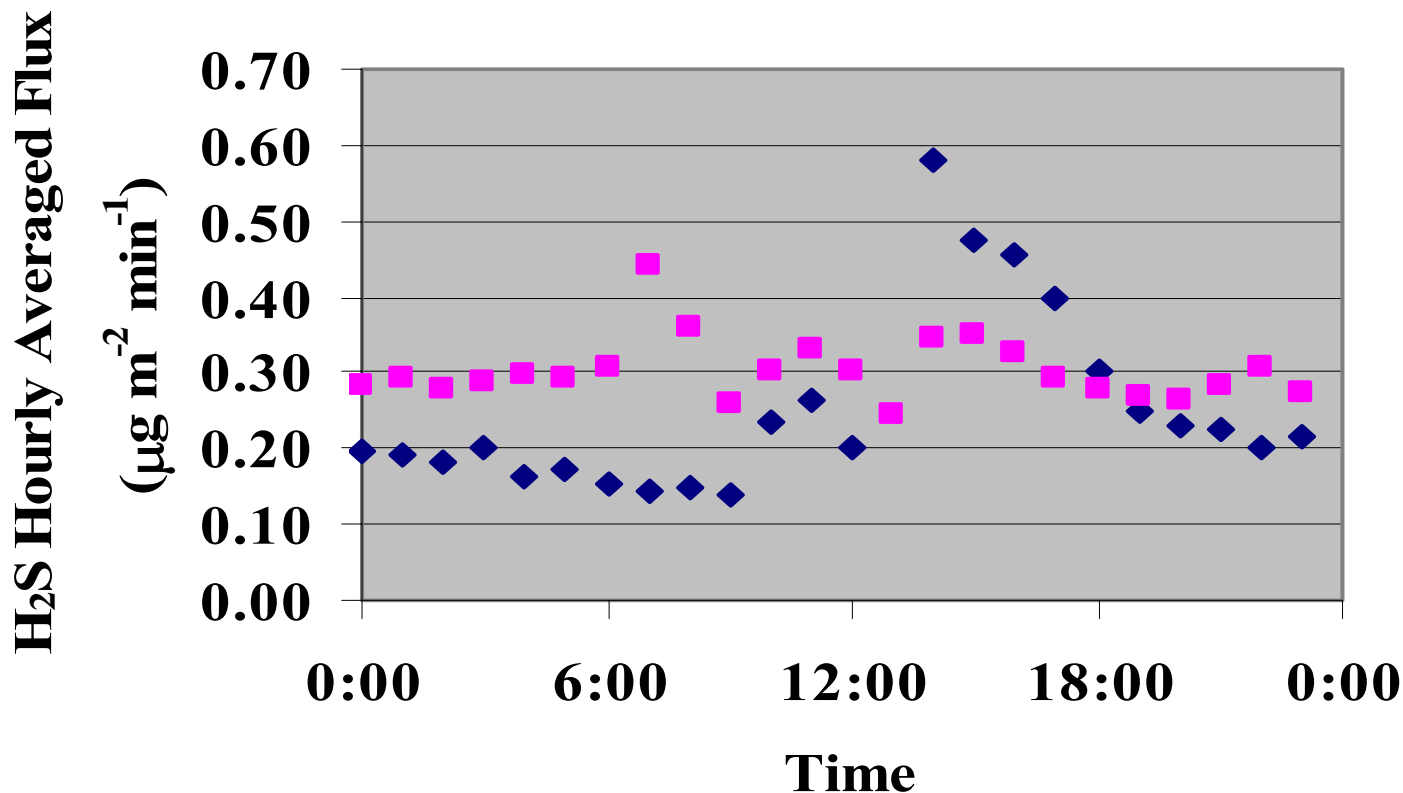
Source: Snoeyink and Jenkins (1980)

Comparison of Ammonia Flux vs Lagoon Temperature



Preliminary Results

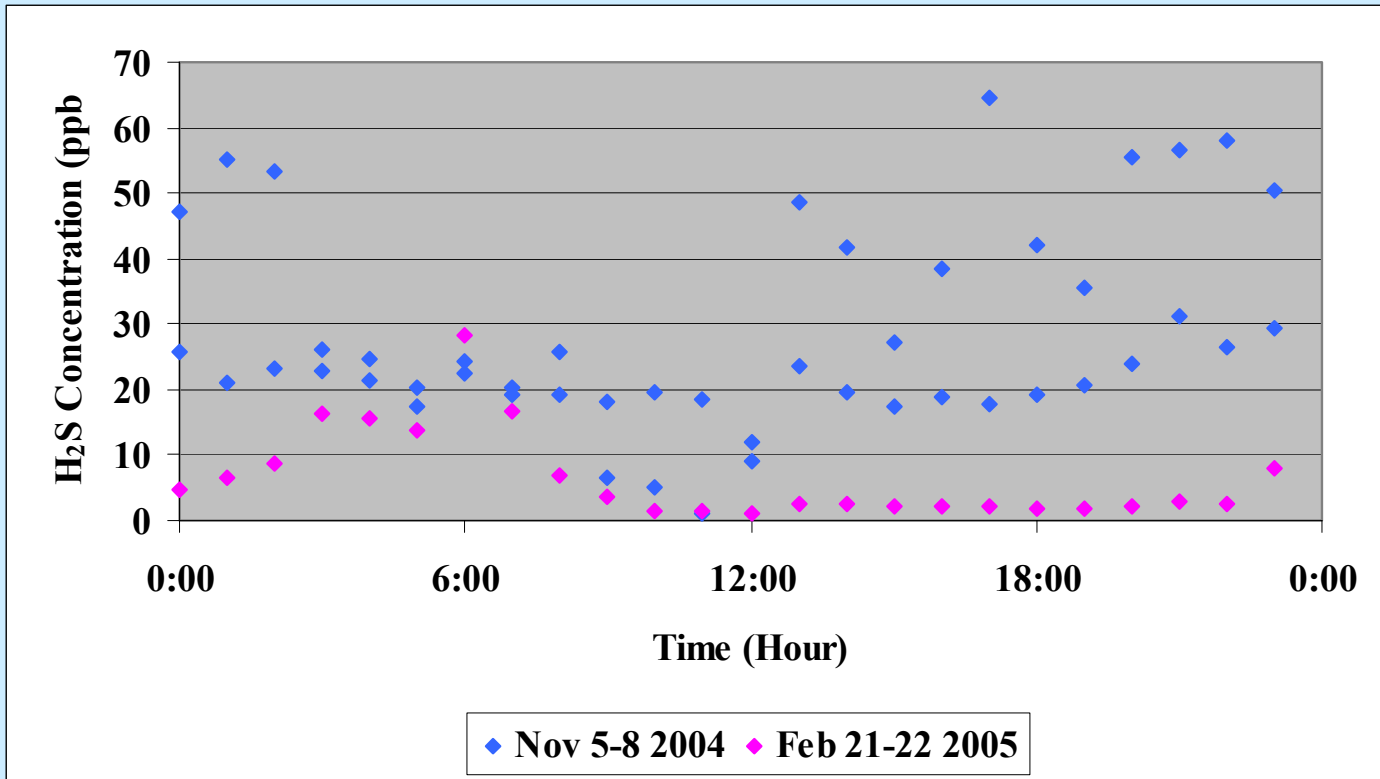
H₂S Lagoon Emissions ($\mu\text{g m}^{-2} \text{min}^{-1}$) Diurnal and Seasonal Variation



◆ Oct 26-Nov 1 2004 ■ Feb 15-22 2005

Preliminary Results

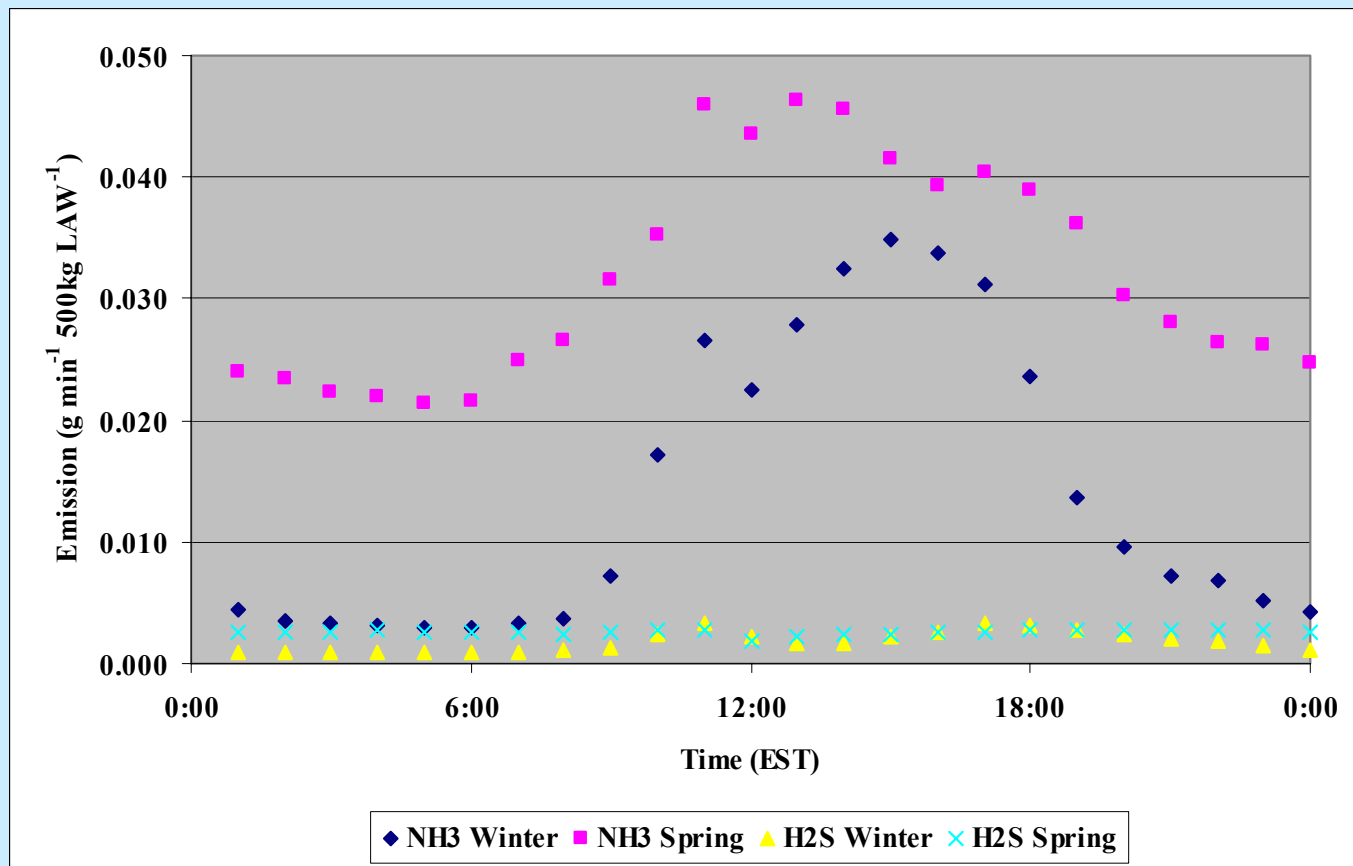
H₂S 10 m Ambient Concentration* (ppb) Diurnal and Seasonal Variation



***Measurements made near hog barns and waste treatment storage lagoons.
Ambient level rules generally apply near property boundary line.**

Preliminary Results

Experimental Site NH_3 and H_2S Barn Emissions Diurnal and Seasonal Variation



- 5 outlet fans per house: 2 - 36", 3 - 48"
- 5 different "on/off" stages for fan usage (Temperature dependent)
- "On/off" stages and fan rpms are monitored and used to calculate H_2S emissions

NRI Air Quality – Extension & Outreach

2004 Progress

- Meetings (two planned & completed)
 - Producer meeting (Hog production and air quality), Jones Co., 20 (October)
 - Regional Pork Conference (Air quality and emissions research update), Kinston, Lenoir Co., 125 (November)
- Trainings with air quality components (two planned & one completed)
 - Hose drag waste applicator impacts on ammonia and odor, 20 (May)
 - Low odor, low drift options for waste water applications - canceled due to low enrollment
- Fact sheets (two planned & one published)
 - Liquid manure application using hose drag method, published
 - Poultry litter amendments, in review
- Web-related activities
 - Expand and strengthen the air quality component of Biological & Agricultural Engineering Dept. Extension website
 - Develop material for web site for the extension component of the Project

NRI Air Quality – Extension & Outreach

2005 Plans

- Meetings (two planned)
 - NC Pork Council, NC Poultry Federation, producer meetings
 - Two producer meetings scheduled to discuss the EPA Air Compliance Agreement
- Trainings with air quality components (two planned)
 - Hose drag waste applicator impacts on ammonia and odor, 20 people (May)
 - Low odor, low drift options for waste water applications - canceled due to low enrollment
- Fact sheets (one planned)
 - Poultry litter amendments (S. Shah, P. Westerman, & J. Parsons), in review
- Web-related activities (continue activities from 2004)

Publications and Presentations

Publications

Aneja V., D. Niyogi, P. Roelle, 2005, An integrated perspective on assessing agricultural air quality, *Intrnl. J. of Global Environmental Issues*, in press.

Niyogi D., K. Alapaty, S. Phillips, V. Aneja, 2005, Considering ecological formulations for estimating deposition velocity in air quality models, *Intrnl. J. of Global Environmental Issues*, in press.

Aneja, V., J. Blunden, C. Claiborn, and H. Rogers, 2005, Dynamic atmospheric chamber systems: applications to trace gas emissions from soil and plant uptake, *Intrnl. J. of Global Environmental Issues*, in press.

Goetz, S., Y. Zhang, and V.P. Aneja, 2005, Measurement, analysis, and modeling of fine particulate matter in Eastern North Carolina, *Atmos. Environ.*, submitted.

Presentations

Aneja, V., J. Blunden, C. Claiborn, and H. Rogers, Dynamic chamber system to measure gaseous compounds emissions and atmospheric-biospheric interactions, NATO Advanced Research Workshop, Environmental Simulation Chambers: Application to Atmospheric Chemical Processes 1 – 4 October, 2004, Zakopane, Poland.

Niyogi D., K. Alapaty, S. Phillips, V. P. Aneja, Considering ecological formulation for estimating deposition velocity in air quality models, AAAR Specialty Conference, Atlanta, 11 – 14 February 2005.

Air Quality: Ray Knighton
NRI Competitive Grants Program
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National Workshop on Agricultural Air Quality: State of the Science

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Rhonda Kranz, Ecological Society of America, Washington, DC

Workshop on Agricultural Air Quality: State of the Science

www.esa.org/AirWorkshop

June 5-8, 2006, Potomac, MD, near Washington, D.C.

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